

Octahedral tilting, monoclinic phase and the phase diagram of PZT

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Abstract. Anelastic and dielectric spectroscopy measurements on $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) close to the morphotropic (MPB) and antiferroelectric boundaries provide new insight in some controversial aspects of its phase diagram. No evidence is found of a border separating monoclinic (M) from rhombohedral (R) phases, in agreement with recent structural studies supporting a coexistence of the two phases over a broad composition range $x < 0.5$, with the fraction of M increasing toward the MPB. It is also discussed why the observed maximum of elastic compliance appears to be due to a rotational instability of the polarisation and therefore cannot be explained by extrinsic softening from finely twinned R phase alone, but indicates the presence also of M phase, not necessarily homogeneous.

A new diffuse transition is found within the ferroelectric phase near $x \sim 0.1$, at a temperature T_{IT} higher than the well established boundary T_{T} to the phase with tilted octahedra. It is proposed that around T_{IT} the octahedra start rotating in a disordered manner and finally become ordered below T_{T} . In this interpretation, the onset temperature for octahedral tilting monotonically increases up to the antiferroelectric transition of PbZrO_3 , and the depression of $T_{\text{T}}(x)$ below $x = 0.18$ would be a consequence of the partial relieve of the mismatch between the cation radii with the initial stage of tilting below T_{IT} .

1. Introduction

In spite of a prolonged and intensive research activity on the ferroelectric perovskite $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (also called PZT 100 $(1-x)/100x$) and related compounds, unsettled issues remain on its phase diagram and on the microscopic mechanisms that make it the most used piezoceramic material in many applications. The highest electromechanical coupling is obtained at compositions $x \lesssim 0.5$, near the morphotropic phase boundary (MPB), which separates the rhombohedral (R) from the tetragonal (T) region in the $x-T$ phase diagram [1, 2]. For decades such a high electromechanical coupling had been attributed to a coexistence of R and T domains near the MPB, with consequent ease for polarisation to change direction through domain switching or domain wall motion. In 1999 Noheda *et al.* [3] found that below the MPB of PZT 52/48 the structure is monoclinic (M), intermediate between R and T. This discovery stimulated extensive investigations to better characterize such an intermediate phase, where the direction of the polarisation can in principle rotate continuously between the T $\langle 001 \rangle$ and R $\langle 111 \rangle$ directions; this provides an appealing explanation to the enhanced ease for polarisation to change direction under an external stress or electric field at the MPB. Yet, there is no consensus on the nature and even existence of the M phase, with a range of alternatives from its existence as uniform phase in a narrow composition range, the coexistence with the R phase in a broader range, or actually a fine mixture of R and T domains or finely twinned R domains behaving on the average as monoclinic. The debate has been recently reviewed [4, 5, 6], and involves the mechanisms of rotation and switching of the polarisation.

The situation is confused also on the Zr-rich end of the phase diagram, where the ferroelectric R phase approaches the antiferroelectric orthorhombic one. Here electron, but not neutron or x-ray, diffraction experiments reveal superlattice peaks incompatible with the R structure, variously attributed to rotations of the O octahedra [7, 8] or to antiferroelectric-like cation displacements away from the average $\langle 111 \rangle$ direction [9, 10].

Structural studies in these critical composition ranges face the problem of analysing structures of domains with very short coherence lengths and possibly of different coexisting phases, so that information from other techniques, although not providing direct information on the cell symmetry, may prove useful in clarifying some issues. We present anelastic and dielectric spectroscopy measurements, which provide new insight in these debates, and we attempt to rationalize the phase diagram of PZT regarding the tendency of the O octahedra to tilt.

2. Experimental and Results

The ceramic samples of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$, with Ti fractions $x = 0.1, 0.14, 0.17, 0.42, 0.45, 0.452$, have been prepared similarly to a previous study [11] with higher values of x (0.455, 0.465, 0.48 and 0.53), with the mixed-oxide method. The starting oxide powders were calcined at 800 °C for 4 hours (700 °C for $x = 0.1$), pressed into bars and sintered

at 1250 °C for 2 h, packed with $\text{PbZrO}_3 + 5\text{wt}\%$ excess ZrO_2 in order to maintain a constant PbO activity during sintering. The powder X-ray diffractograms did not show any trace of impurity phases and the densities were about 95% of the theoretical ones. The sintered blocks were cut into thin bars 4 cm long and 0.6 mm thick, whose major surfaces were made conducting with Ag paint.

The dielectric susceptibility $\chi(\omega, T) = \chi' - i\chi''$ was measured with a HP 4194 A impedance bridge with a four wire probe and an excitation of 0.5 V/mm, between 0.2 and 500 kHz. The heating and cooling runs were made at 0.5 – 1.5 K/min between room temperature and 540 K in a Delta climatic chamber.

The mechanical analogue of the dielectric susceptibility is the elastic compliance $s = s' - is''$, which was obtained as the reciprocal of the dynamic Young's modulus $E(\omega, T) = E' + iE'' = s^{-1}$. It was measured between 100 and 750 K by electrostatically exciting the flexural modes of the bars suspended in vacuum on thin thermocouple wires [12]. During a same run the first three odd flexural vibrations could be tested, whose frequencies are in the ratios 1 : 5.4 : 13.2. The fundamental resonance angular frequency is [13] $\omega \propto \sqrt{E'}$, and the temperature variation of the real part of the compliance is given by $s(T)/s_0 \simeq \omega_0^2/\omega^2(T)$, where ω_0 is chosen so that s_0 represents the compliance in the paraelectric phase. The imaginary parts of the susceptibilities contribute to the losses, which are presented as $Q^{-1} = s''/s'$ for the mechanical case and $\tan \delta = \chi''/\chi'$ for the dielectric one.

2.1. The new phase transformation at T_{IT} for $x \sim 0.1$

Figure 1 presents the anelastic spectrum of PZT 90/10. The peak in both real and imaginary parts of the compliance at $T_{\text{C}} = 532.7$ K, with 1.6 K hysteresis between heating and cooling, signals the transition between cubic paraelectric and ferroelectric phase, while the anomaly at $T_{\text{T}} = 368$ K with an hysteresis of 1 K corresponds to the transition from the rhombohedral $R3m$ (R) to the tilted $R3c$ (R_{L}) phase, often labelled as R_{H} and R_{L} respectively. These temperatures fall exactly on the well known phase diagram of PZT, as shown in figure 6 below. There is however an additional broad step in s' , without any counterpart in Q^{-1} , at the temperature $T_{\text{IT}} \simeq 477$ K, which we identify as the onset of an intermediate tilt pattern of the octahedra, before the final tilt pattern develops below T_{T} .

A signature of this new transition is present also in the dielectric susceptibility as a broad step in $\tan \delta$ and a hardly discernible hump in χ' . This is shown in figure 2, together with the anomalies at T_{C} and T_{T} . The dashed arrows in figure 2 are the transition temperatures deduced from the anelastic spectra in figure 1. The elastic compliance is peaked at a somewhat lower temperature than the dielectric susceptibility at the ferroelectric transition, as already observed [14], and the same is true for the tilt transition, but it should be noted that since the two susceptibilities are differently coupled to the order parameter, the shapes of their anomalies have to be different from each other.

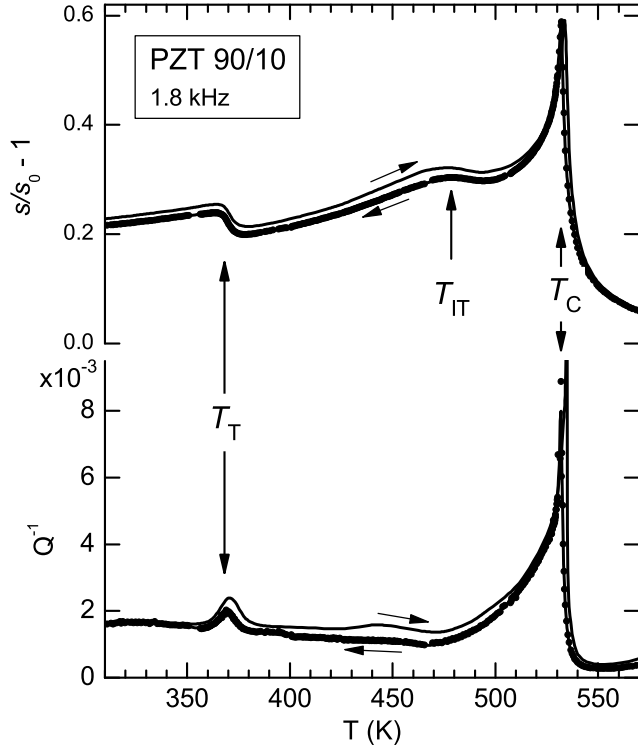


Figure 1. Anelastic spectrum of PZT 90/10 measured at 1.8 kHz during heating and cooling.

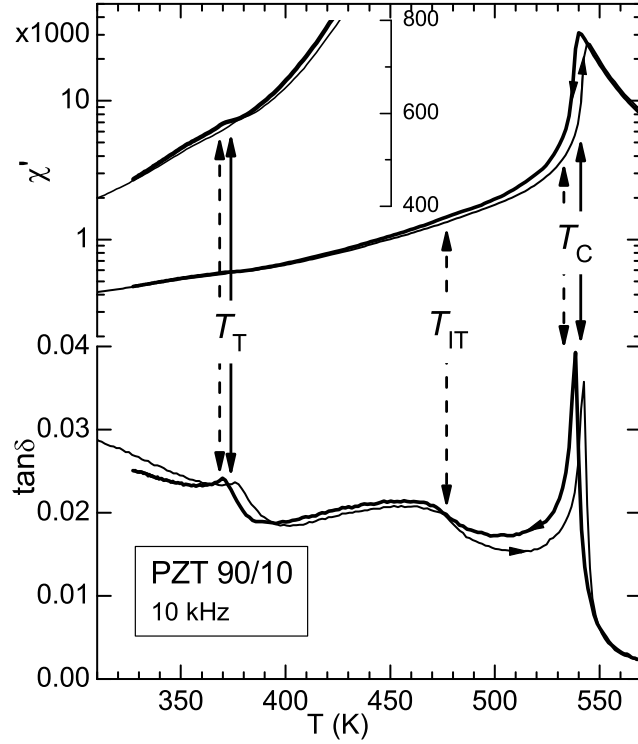


Figure 2. Dielectric spectrum of PZT 90/10 measured at 100 kHz during heating and cooling. The dashed arrows are the transition temperatures deduced from the anelastic spectra.

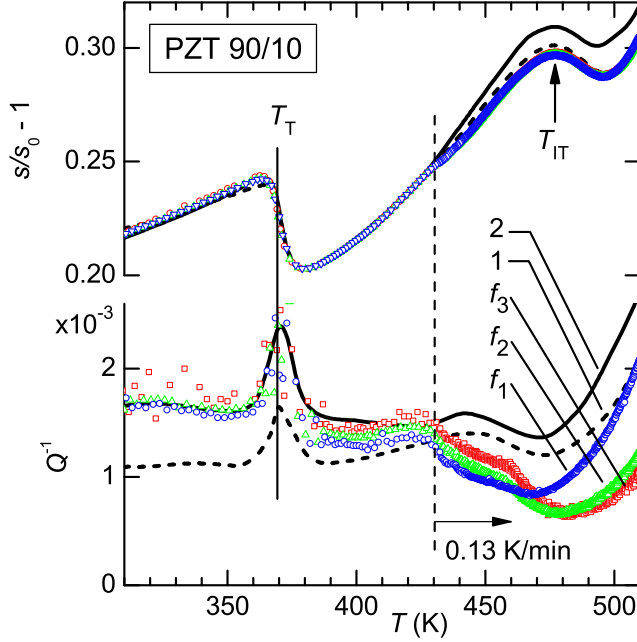


Figure 3. Anelastic spectra of PZT 90/10 measured during heating. 1 (dashed): poled state, 1.8 kHz; 2 (solid): subsequent run (unpoled) at 3 ± 1 K/min, 1.8 kHz; $f_1 - f_3$: subsequent run slowed down to 0.13 K/min above ~ 430 K (dashed vertical line) measured at $f = 1.8, 9.7$ and 24 kHz.

In order to check that there is indeed a structural transformation at T_{IT} , we verified that the step in $s'(\omega, T)$ is independent of the measuring frequency $\omega/2\pi$, temperature rate and polarisation state. In fact, the susceptibility curves may be affected by various processes, especially in the presence of strong domain wall relaxations, as is the case below the ferroelectric transition. When the temperature rate is such that the domain configuration is kept far from equilibrium, the susceptibility curve generally drops when the temperature rate is decreased and partial aging proceeds. This occurs also in certain temperature and composition ranges of PZT, where marked irregularities may be induced in the $s(\omega, T)$ curves by varying the temperature rate. We will not discuss such phenomena, and only mention that they can be reduced by keeping the temperature rate as constant and low as possible, and their amplitude is larger at lower measuring frequency.

Figure 3 shows that the anomaly at T_{IT} is instead perfectly reproducible and independent of all these variables. Curve 1 (dashed) was measured in the initially polarised state of the sample, obtained by application of 3 kV/mm at 120 °C for 40 min. The temperature rate was +1.3 K/min, except near T_T , where it was lowered to 0.8 K/min in order to get enough accurate and closely spaced data points; the run was extended up to 580 K, hence losing the polarisation. Curve 2 (solid) is the subsequent heating run at 3 ± 1 K/min. The imaginary part is always above the previous run both because of the higher density of relaxing domain walls in the unpoled state, and because at the higher temperature rate such walls are more out of equilibrium. Yet, the real

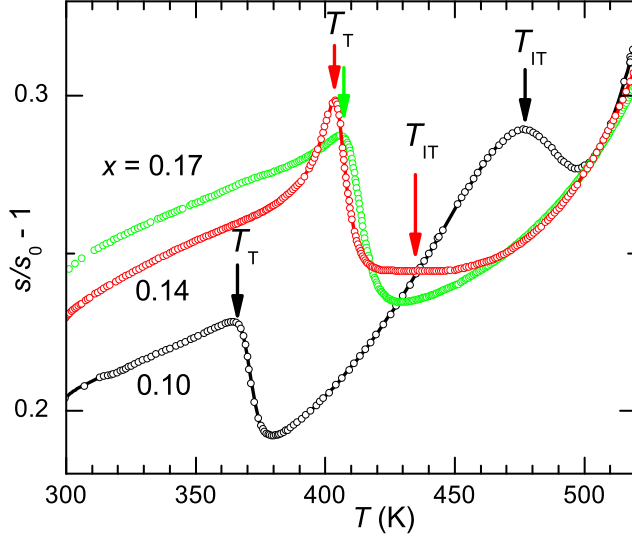


Figure 4. Anelastic spectra of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ with $0.10 \leq x \leq 0.17$ measured at 1.8 kHz during heating.

parts are practically coincident until ~ 430 K, where they start slowly departing from each other due to the increasing influence of the ferroelectric domain wall relaxation. The other three curves (empty circles) were measured during the third heating run at 2–3 K/min until ~ 430 K and 0.13 K/min above that temperature; the frequencies are $f_1 = 1.8$ kHz, $f_2 = 9.7$ kHz and $f_3 = 24$ kHz. The important point is that both steps at T_T and T_{IT} are practically the same in all the s' curves. This is true also for the peak in Q^{-1} at T_T , while the differences in the $Q^{-1}(\omega, T)$ curves at higher temperature and particularly the drop when the rate is lowered to 0.13 K/min have to be attributed to the tail of the domain wall relaxations below T_C . There is an additional peak or kink around 445/460 K in the $Q^{-1}(\omega, T)$ curves, which does not appear to be connected with anomalies in the real part and will be ignored. The lack of a peak in Q^{-1} at T_{IT} and the independence on frequency of the step in s' also exclude that the anomaly is caused by relaxation of any type of defects. Figure 3 therefore demonstrates that at the origin of the anomaly at T_{IT} there is a somewhat broadened but otherwise well behaved phase transformation. We will consider T_{IT} as the temperature of the upper edge of the rounded step in $s'(T)$, analogously to T_T , where the assignment is corroborated by the neat peak in $Q^{-1}(T)$.

In order to draw a T_{IT} line in the phase diagram, we also measured the two concentrations $x = 0.14$ and 0.17 , whose compliances are plotted together with that of $x = 0.10$ in figure 4. The step at T_T shifts to higher temperature according to the usual phase diagram, though it acquires a peaked component, particularly evident at $x = 0.14$, while the broader step at T_{IT} shifts to lower temperature merging with T_T . That an anomaly exists for $x = 0.14$ around 430 K is evident by comparing with the curve of $x = 0.17$. Both curves are practically coincident above 470 K and run parallel to each other below the step at T_T , but the $x = 0.14$ curve has a clear bump

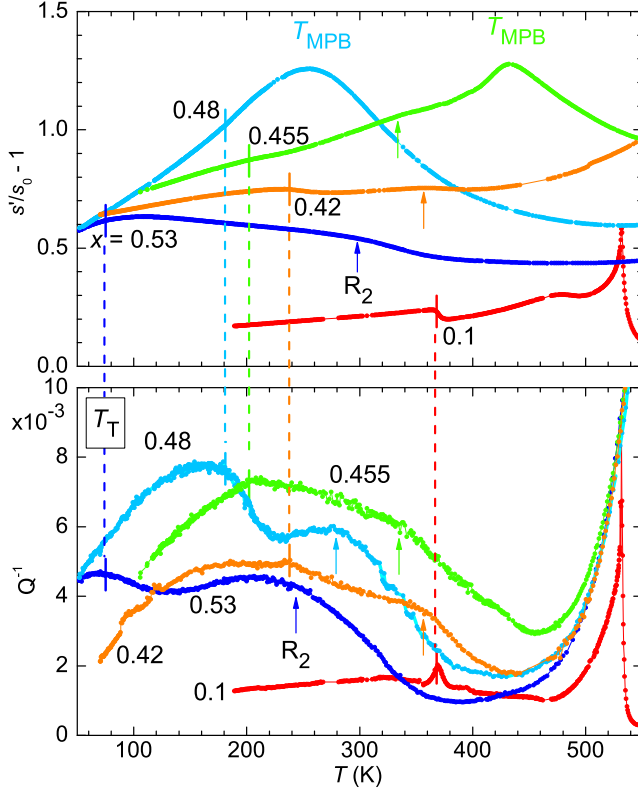


Figure 5. Anelastic spectra of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ with $x = 0.1, 0.42, 0.455, 0.48$ and 0.53 measured at $1 - 1.8$ kHz. The vertical lines mark T_T , while the arrows the relaxation R_2 (the three highest x are from reference [11]).

indicated by the arrow, whose precise shape is however difficult to evaluate. An even more attenuated anomaly might exist also for $x = 0.17$, even closer to T_T , but it is not actually distinguishable.

2.2. Compositions near the MPB

The measurements on the samples at higher Ti content are similar to those already published [11] and a selection of them, including some from reference [11], is presented in figure 5. With increasing x , the anomaly at T_T , marked by vertical lines, becomes more diffuse and the spike in Q^{-1} gradually transforms into a step of increasing amplitude, at least until it occurs into the R/M phase, when $x < 0.5$. This is consistent with the observation of a diffuse tilt transition by neutron diffraction in PZT 60/40 [15, 16]. The step in s' , instead, decreases its amplitude and becomes hardly visible due to the peak at T_{MPB} . The latter has been attributed to the ability of the polarisation to continuously rotate in the M phase between the T and R directions [11]. The analysis of the anomaly at T_T is also hindered by a broad peak in the losses around $200 - 350$ K, labelled R_2 in reference [11], and whose frequency dispersion indicates a relaxational origin rather than a phase transformation. It appears also as a frequency-dependent hump in s' and is

indicated by arrows in figure 5 (the dependence on frequency is not shown). The curves with $x = 0.45, 0.452, 0.455$ and 0.465 are very similar to each other, with T_T signaled by a weak step in $s'(T)$ and a small cusp in $Q^{-1}(T)$, which at first appear as qualitatively different from the clear step in Q^{-1} at $x = 0.48$. The difference in the $Q^{-1}(T)$ curves, however, may be less important than it appears, because one must take into account the maximum R_2 , which loses importance with respect to the spike/peak at T_T on approaching the MPB. It is therefore possible that, if one were able to decompose the curves into the two contributions, R_2 and the anomaly at T_T , the latter would result as a broadened step already at $x \simeq 0.46$.

3. Discussion

Figure 6, presents the commonly accepted phase diagram of PZT [1, 17] (solid lines) together with the points deduced from our anelastic spectra, including those of reference [11]; the dashed lines pass through our data and are drawn as explained in the following paragraphs, but further measurements are necessary in order to confirm their exact shape. The new anelastic and dielectric experiments presented here contain essentially two results: the existence of a novel phase transformation at T_{IT} below $x \sim 0.17$ and the confirmation that there is a perfect continuity of the $T_T(x)$ line of the onset of octahedral tilting up to the MPB, while T_T in the T phase is lower than the extrapolation from the MPB.

The phases are the following: C is paraelectric cubic $Pm\bar{3}m$, O is antiferroelectric (AFE) orthorhombic $Pbam$ with the octahedra rotated of the same angle in anti-phase along the pseudocubic directions [100] and [010] ($a^-a^-c^0$ in Glazer's notation[19]) and antiferroelectric shifts of the cations along [110] [20, 10]. All the other phases are ferroelectric (FE), those just below the Curie temperature T_C having unrotated octahedra: T is tetragonal $P4mm$ with polarisation along [001], R is rhombohedral $R3m$ with polarisation along [111], M is monoclinic Cm with the polarisation along a direction intermediate between T and R. Below the T_T border the octahedra rotate giving rise to R_L rhombohedral $R3c$ ($a^-a^-a^-$), T_L tetragonal $I4cm$ with tilt pattern $a^0a^0c^-$, as predicted by first principle calculations [21] and recently verified by neutron diffraction at 5 K [22], M_L monoclinic Cc with tilt pattern $a^-a^-b^-$ intermediate between R_L and T_L . The nature of the monoclinic phases, highly debated, and of the new intermediate phase $(R+M)_I$ are discussed next.

3.1. MPB and search for the R/M border

The phase diagram proposed by Noheda *et al.* [17, 18], and since then commonly adopted and reproduced with first principle calculations [21], contains an almost vertical border between the R and M phases within the MPB range at $x_{R/M} \simeq 0.455$ (dotted line in figure 6), but the presence of this border is contradicted by recent neutron diffraction experiments. The results of one of them [16] are much better refined in

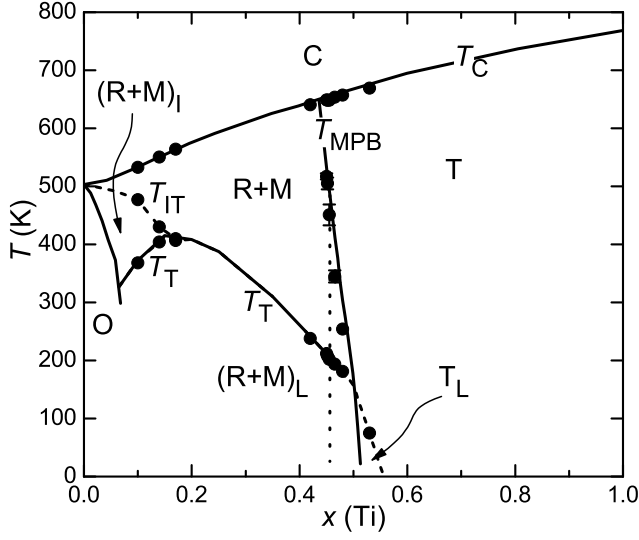


Figure 6. Phase diagram of PZT with the following phases: C paraelectric cubic $Pm\bar{3}m$, O antiferroelectric orthorhombic $Pbam$; all the other phases are ferroelectric: T tetragonal $P4mm$, T_L tilted tetragonal $I4cm$, R+M mixed rhombohedral $R3m$ + monoclinic Cm , (R+M)_L mixed tilted rhombohedral $R3c$ + monoclinic Cc , (R+M)_I rhombohedral + monoclinic with intermediate tilt. The filled circles are the transition temperatures deduced from our measurements here and in reference [11]. The dashed lines are proposed here and the dotted vertical line is the R/M boundary proposed by Noheda [17, 18].

terms of monoclinic Cm rather than R structure at $x = 0.4$, well within the supposed R region. In the other experiment [6] it is established that in ceramic samples the R and M phases coexist over the whole composition range from the orthorhombic (O) phase to the MPB, with the fraction of M phase increasing toward the MPB. The actual relative fraction of the two phases, and some details of the atomic displacements depend on the preparation technique and a pure R phase can be obtained in single crystals, only available at $x \leq 0.1$ [6, 23, 24]. In addition, there is considerable debate about the role of the short length scale of the T, R and M domains near the MPB [25] and of the high density of domain boundaries or microtwinning of the R domains, that may constitute an adaptive phase with the average properties attributed to the M phase [26, 27, 28, 29, 22, 30]. First principle calculations do not solve the issue, since in some studies a stable monoclinic ground state is found [31] but in other cases is excluded [32, 33].

In our data there is no sign of an R/M border, at least within the interval $0.42 < x < 0.48$. In fact, the $T_T(x)$ line is perfectly continuous within that interval, and the anelastic spectra exhibit a smooth evolution from $x = 0.42$ to $x = 0.465$ and probably also 0.48, as discussed in the explanation of figure 5. Moreover, the anelastic spectra do not have any sign of an additional M/R phase transition, expected if the M/R border existed for $x > 0.42$ and were not vertical, as in the theoretical phase diagram obtained from first-principle calculations [21].

For all these reasons we labelled the region to the left of the MPB as R+M, adopting the view of Yokota *et al.* [6] of a mixture of rhombohedral $R3m$ and monoclinic Cm phases, both with untilted octahedra. When discussing the $x = 0.1$ composition, however, we will for simplicity refer to the R phase only, which certainly predominates over the M one. Of course, the absence of a M/R boundary is natural in the hypothesis that the M phase is actually the average of an adaptive microtwinned R phase.

3.2. *M versus R/T adaptive phase*

The different conclusions of the various analyses based on thermodynamic approaches and first principle calculations probably reflect the fact that the border between a true M phase and an adaptive one is indeed vague. The MPB is the locus in the phase diagram where the anisotropy of the free energy changes over from stabilizing the R phase to the T phase. The main anisotropic term in the Landau expansion in terms of powers of the polarisation \mathbf{P} is $\propto (P_1^4 + P_2^4 + P_3^4)$ or its complementary $(P_1^2 P_2^2 + P_2^2 P_3^2 + P_3^2 P_1^2)$, with extrema in the $\langle 100 \rangle$ or $\langle 111 \rangle$ directions, depending on the sign, which stabilize the R or T phase. Including terms of the sixth order, the anisotropy acquires extrema also along directions stabilizing the O phase, while it is necessary to include eighth order terms in order to stabilize the M phase [34]. At the MPB the anisotropic term of fourth order changes sign and therefore vanishes [35, 36]: the material is isotropic with respect to polarisation, at least up to the fourth order in \mathbf{P} , and one has a transversal or rotational instability of \mathbf{P} [37] accompanied by divergence of the transversal dielectric susceptibility and some enhancement of the corresponding shear compliance s_{44} [38]. A divergence of the compliance can be obtained at the transition between T and O phase, including the sixth order terms [38], but this is not the case of PZT, which does not have a O phase at the MPB. The theoretical expressions of the compliances from an expansion of the free energy up to the eighth order are certainly cumbersome, but it is not necessary to work them out in order to establish that a divergence of s_{44} is expected also at the T/M border. In fact, we argued [11] that in the case that a M phase exists in which \mathbf{P} can continuously tilt from the T to the R directions with little change of the magnitude, the rotation angle from the original T direction acts as order parameter [39] and is almost linearly coupled to the strains of symmetry Γ_{5-} (ε_4 , ε_5 and ε_6 in Voigt notation), thereby causing a divergence in the respective compliance s_{44} [40, 41]. Accordingly, we interpreted the maximum in the compliance at the MPB, particularly pronounced at $x = 0.465$, as due to this rotational instability in the M phase [11].

The main arguments against a true M phase are that it is very unlikely that PZT is so anharmonic to require terms up to the eighth power of \mathbf{P} in the expansion of the free energy [30, 36]. As a consequence, the real structure should be R, but with fine twinning thanks to the near isotropy at the MPB, which lowers the energy of the domain walls. Such an adaptive phase, analogous to the heavily twinned phases in martensites, would produce diffraction patterns easily confused with a homogeneous M phase and would also cause extrinsic softening [30, 36]. The first part of the argument is certainly

convincing for an ideal homogeneous crystal, but PZT has both quenched strain fields from the cation disorder [34] and also internal fields from the domain configuration, which presents particularly wavy and strained walls in the R phase [28]. While these microstructure and internal strains may let the diffraction patterns of the R phase appear as an homogeneous M phase, they also modify the local anisotropy, acting as higher order terms in the free energy expansion and stabilizing an M phase [34]. We would therefore expect that there are regions where a real M phase is formed, although with cell parameters and direction of the polarisation dependent on the local field. A border between a mixed M+R [6] and a polar glass state [30] is probably impossible to establish, and the balance between the two descriptions may also depend on the sample preparation and microstructure, not to mention whether the sample is bulk ceramic or thinned for electron microscopy.

Here we would like to point out an aspect that distinguishes between M, not necessarily homogeneous, and microtwinned adaptive R phase and is overlooked in the debate: the dynamics. In fact, an adaptive phase with high density of domain walls having vanishing energies causes extrinsic softening [30, 36], but we are not aware of a detailed theory of its frequency and temperature dependence. We would expect an important contribution of relaxational nature, with a consequent dependence on frequency, and possibly also nonlinear response, none of which we observe [11]. Certainly a complicated and fine domain structure exists, and it may well be at the origin of the nonlinear stress-strain response of PZT [30, 42], but the elastic response to low amplitude excitation that we measure is strictly linear and almost frequency independent. Again, the border between extrinsic softening from fine twinning and intrinsic linear softening due to a rotational instability may be blurry, since the vanishing of the orientational free energy barrier brings about a crossover from thermally activated, characteristic of domain walls, to almost athermal dynamics, but the peak in s' at T_{MPB} is more characteristic of the latter.

3.3. The octahedral tilt transition

From the present experiments we are not able to establish whether the tilting transition affects both M and R domains in the same manner or not, because we are not able yet to interpret the evolution of the shape and amplitude of the anomaly at T_{T} with varying x (figure 5), whose analysis is also made difficult by the relaxation R_2 (figure 5).

We would like to stress the different origin of the hump corresponding to R_2 with respect to the anomalies at T_{T} and T_{IT} , since they all appear similar in the $s'(T)$ curves, and it may be tempting to identify R_2 as another structural transition, for example tilts in the M phase instead of the R phase. A more careful examination, however, indicates that this is not the case. The anomalies at T_{T} and T_{IT} have all the characteristics of well behaved, though diffuse, structural transformations, as described above and in reference [11] for T_{T} : they are perfectly reproducible during heating and cooling, and are independent of frequency and temperature rate. Instead, R_2 has none of these

characteristics: its amplitude is larger at lower frequency and strongly depends on the temperature rate (data not shown here), so that we attribute it to kinetic effects of the rearranging ferroelectric domain walls or adaptive microtwins, rather than to a phase transformation. A final argument against the involvement of octahedral tilts in the relaxation R_2 is that it is observed also in the T phase just below ~ 300 K (curve $x = 0.53$ in figure 5), where tilting has never been observed.

The tilted tetragonal phase is predicted to have $I4cm$ space group, based on first-principle calculations [21] and recent neutron diffraction observations [22]. A cell doubling transition in the T phase, possibly due to an octahedral anti-phase rotation, was proposed by Ragini *et al.* [43], after the observation in PZT 48/52 of superlattice peaks below 189 K and anomalies in the dielectric χ' and resonance frequency, but the temperature of such anomalies is definitely higher than the T_T we found at the same composition [11]. We cannot exclude that the technique of sample preparation has an influence on the position of the $T_T(x)$ line in the high x region, considering that it may affect the fraction of R and M phases [6].

In figure 6 we drew the $T_T(x)$ line straight until the MPB and then again straight with a higher slope in order to interpolate the only available point in the T phase (dashed line). Such a kink at the MPB is not actually observed; it might be either smoother or a more discontinuous step and future work is necessary in order to clarify this point.

3.4. $T_T(x)$ border and tolerance factor

The occurrence of tilting transitions of the BO_6 octahedra is an extremely common phenomenon in ABO_3 perovskites, and it has been rationalized in terms of the tolerance factor [44, 45]

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad , \quad (1)$$

which is 1 if the mean ionic radii, usually taken from Shannon's tables [46], exactly match the A-O and B-O lengths in a cubic cell. When $t < 1$, the B-O bond is too long with respect to the A-O one; hence the A-O-A network exerts a compression over the network of octahedra, which rotate in order to accommodate the mismatch while keeping the B-O bonds long. The A-O bonds are $\sqrt{2}$ longer and therefore are weaker and have larger thermal expansion than the B-O bonds; therefore t always decreases on cooling, and when it drops below a critical value, within the interval $0.97 < t < 1$ for most perovskites [47], a tilting transition occurs. The tolerance factor can also be decreased in a solid solution by increasing the mean ionic radius in the B sublattice or decreasing that in the A sublattice. Moreover, a sequence of tilting transitions may occur with proceeding cooling and/or changing of the ionic radii, usually through more symmetrical tilt patterns first, like rhombohedral $a^-a^-a^-$, and then to the more distorted orthorhombic patterns [44, 45]. This framework is widely adopted to explain the phase diagrams of all types of perovskites with chemical substitutions, including the ferroelectric ones [10, 48] and even in the presence of O vacancies [49], and PZT

is no exception. The Shannon radii of Ti and Zr in octahedral coordination are 0.605 and 0.72 Å, respectively, yielding $t = 1.027$ for PbTiO_3 , which indeed undergoes below T_C off-centering of Ti in too large and untilted octahedra, to $t = 0.97$ of PbZrO_3 , which undergoes a $a^0b^-b^-$ tilt transition with AFE shifts of the cations [50], having passed through the more symmetrical rhombohedral $a^-a^-a^-$ structure at intermediate compositions. Conforming to the above discussion, the $T_T(x)$ line encloses the region of low tolerance factor, namely low T and low x , possibly with some discontinuity when passing from the T to the R+M region, from $x > 0.5$ down to $x = 0.18$. At this point it does not prosecute to the maximum value at $x = 0$, but decreases sharply. The departure from the expected monotonic rise has been already noted and explained in terms of competition between the O AFE phase with $a^-a^-c^0$ tilt and the R FE phase; this would cause a frustration of the Pb displacements and consequently inhibit octahedral tilting, which is coupled with such displacements [10].

The presence of a phase transition at a $T_{IT}(x)$ merging with $T_T(x)$ around $x \sim 0.17$ alternatively suggests that the phase $(\text{R}+\text{M})_I$, in addition to the cation shifts away from [111], has an initial stage of octahedral tilting. In other words, if a structural transition occurs in that temperature range, it seems more likely that its driving force acts on the octahedral tilting rather than on antiferroelectric cation shifts. In this manner the depression of the boundary of the $R3c$ phase is a consequence of the fact that the mismatch between (Ti/Zr)-O bonds and Pb-O bonds has been relaxed by the first tilting transition at T_{IT} , and further cooling below T_T is necessary in order to trigger the final $a^-a^-a^-$ pattern. In this view, the frustration between the FE and AFE phases would mainly broaden and split in two stages the tilting transition, and the depression of the combined $T_{IT} - T_T$ line near $x = 0.17$ is much less important than that of the T_T curve alone. The existence of coupling between tilts and polar modes is recognizable by the effect of the transition at T_T on the polarisation [51, 52], and dielectric susceptibility [8] (see also the present data), by the reduction of the extrinsic contribution to piezoelectric effect in the tilted $R3c$ phase [53] and is also indicated by first-principle calculations [54].

3.5. Nature of the intermediate phase below T_{IT}

We can only make conjectures on the nature of the transition at T_{IT} based on our susceptibility experiments. If it is indeed an initial stage of the rotations of the octahedra, it may be a tilt pattern intermediate between those of the O and R_L phases, like $a^-a^-b^-$ [10], or it may involve the M_3 in-phase rotation modes [8, 55]. Indeed, although no experimental phonon-dispersion data are available for PbZrO_3 [56], first-principles calculations indicate that the whole $R_{25} - M_3$ branch is unstable, and not only the R_{25} mode of anti-phase rotations [57]. It is therefore possible that a combination of the two types of instabilities produces a relatively disordered tilt pattern, which becomes the ordered $a^-a^-a^-$ ($R3c$) or $a^-a^-b^-$ (Pc) structure below T_T . The concept of disordered tilts has been proposed for explaining why the techniques providing snapshots of the local structure, the X-ray absorption spectroscopies EXAFS and XANES and the

pair distribution function from neutron diffraction, do not see any change at the tilt transitions of perovskites like NaTaO_3 [58] and the same PZT [59]. The situation is similar for most of the apparently displacive transformations in perovskites involving off-centering of cations, like the FE transitions in BaTiO_3 and PbTiO_3 . The issue has been solved by assuming that those transitions have an important order-disorder component, so that the Ti atoms are off-center also in the cubic phase, but without correlation between different cells [60, 61]. The application of the same concept to the transitions involving concomitant rotations of the octahedra about more than one direction is less obvious, since completely disordered tilts would require excessive distortions of the octahedra. Yet, the idea that the phase $R3m$ of PZT is untilted on the average but locally tilted has been adopted by other authors [7, 8], also to justify the fact that first principle calculations indicate the tilted $R3c$ structure and not the $R3m$ one as the ground state of PZT [54]. In our case, the hypothesis that the initially disordered tilting below T_{IT} becomes long range ordered below T_{T} provides a rationale for the different aspects of the two anomalies: the one at T_{IT} is diffuse due to the dynamical frustration of the tilts, while that at T_{T} is sharp.

Although the transition at T_{IT} had never been reported before, the existence of an additional phase of still controversial nature in the PZT phase diagram near the boundary to the O phase is indicated by electron diffraction experiments. In such experiments, $\frac{1}{2}\{k\ell 0\}$ reflections have been observed near room temperature, which are incompatible with both the O and R phases, and have first been attributed to in-phase tilting of the octahedra [7]. Later, it has been argued that rotations or distortions of the O octahedra would not be sufficient to produce spots with the observed intensities [9]; moreover, in-phase rotations would not produce reflections with $h = k$, which are instead observed, and are generally unlikely to occur in perovskites with t only slightly smaller than 1 [10]. The superlattice reflections have therefore been attributed to antiferroelectric shifts of Pb away from $\langle 111 \rangle$ in the $\langle 110 \rangle$ directions, as in the neighboring AFE O phase. A difficulty in characterizing the new structure is that the superlattice reflections are observed only in electron diffraction, but not in X-ray and neutron diffraction [9]; possible reasons are small scattering intensities due to the different cross sections in the different techniques, and the occurrence of these atomic displacements as surface effects in the very thin samples used for TEM [9]. Nonetheless, a narrow region of intermediate phase between the AFE O and the FE R phases has been proposed [10], untilted Pm at higher temperature and tilted Pc below the usual T_{T} border. According to this phase diagram, T_{IT} would correspond to the transition from $R3m$ to Pm .

While the present measurements on ceramic samples prove that the presence of an intermediate phase below T_{IT} is a bulk phenomenon, we feel that the question whether the transition involves only cation shifts or also octahedral rotations is yet open, in view of the expected small intensity of reflections connected with O shifts [9]. The issue should be clarified by careful neutron diffraction experiments, which are more sensitive to O displacements and do not involve the uncertainties connected with very

thin samples where surface effects are important and the actual temperature under the electron beam may be considerably higher than expected.

3.6. Signatures of the transition at T_{IT} in the previous literature

There is abundant literature on PZT near the $x = 0.1$ composition, so that it seems appropriate to examine possible signatures of the transition at T_{IT} in previous studies, which had been overlooked because smaller and less definite than the anomalies at T_T .

A first indication of a transition at T_{IT} comes from a minor step in the steeply falling $P(T)$ curve of PZT 90/10 in figure 6 of reference [24], although it had not been recognized as such, being less clear than the transition at T_T . Also the temperature dependence of the rhombohedral angle $\alpha(T)$ in PZT 90/10 may be re-examined. Such an angle is related to the octahedral tilt angle in the R structure [62], and the lack of clear change of slope of $\alpha(T)$ at T_T was explained [23] as due to dynamic fluctuations of the tilt angle above T_T , an explanation very similar to the assumption of a R_I phase of disordered tilts. The difference is that the tilt disorder in the R_I phase would not be dynamic but almost static with onset around T_{IT} .

The fact that the local symmetry of PZT 90/10 is lower than rhombohedral is confirmed by recent infrared and Raman spectroscopy experiments [55], where several additional modes are observed, besides those of a uniform R phase. Such modes are compatible with the additional disordered Pb shifts in the orthorhombic directions [9, 10] but also with the M_3 in-phase tilt mode of the O octahedra [55], which, together with the anti-phase R_{25} mode, would produce a disordered tilt pattern. In the same study, dielectric susceptibility curves of PZT 90/10 are shown, which are very similar to those of figure 2, except for the lack of a clear anomaly at T_{IT} ; the hump in the imaginary part, however, appears with 2% La doping [55].

4. Conclusions

New anelastic and dielectric spectroscopy experiments are presented on $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ with $0.1 \leq x \leq 0.17$ and $0.42 \leq x \leq 0.452$, providing new information on the phase diagram of PZT at the critical compositions near the antiferroelectric and morphotropic borders. At $x = 0.1$, a new diffuse phase transformation is found at $T_{IT} \sim 480$ K, which is interpreted as the onset of disordered tilting of the O octahedra, before the long-range ordered tilt pattern develops at the well established sharp transition at $T_T = 368$ K. Indications of such a phase transformation from earlier literature are also reported. On increasing Ti content, T_{IT} decreases and merges with T_T around $x \sim 0.17$. In this interpretation, the onset temperature for octahedral tilting monotonically increases from $T_T = 0$ within the Ti-rich tetragonal phase up to the antiferroelectric transition of PbZrO_3 . The well known depression of $T_T(x)$ below $x = 0.18$ would be due to the fact that the mismatch between the cation radii is partially relieved at the initial transition at T_{IT} . The combined $T_{IT} - T_T$ border presents a much shallower depression near $x = 0.17$,

but further anelastic and dielectric experiments at additional compositions with $x < 0.25$ are necessary to clarify the exact shape of the borders of the phase diagram, for example if the T_{IT} line merges with T_T , as depicted in figure 6, or crosses it and prosecutes, as proposed by Woodward *et al.* [10] Yet, the exact nature of the intermediate phase or phases close to the border with the AFE O phase should be clarified by additional diffraction experiments, analysed with the consciousness of the existence of a transition at T_{IT} .

It is discussed why the frequency independent maximum of the linear and elastic compliance at the MPB can hardly be explained by finely twinned R phase alone, and rather indicates the presence of a monoclinic phase, possibly stabilized by the internal random strains and coexisting with the rhombohedral one. The $T_T(x)$ line is also shown to be perfectly continuous up to the MPB, which, together with a smooth evolution of the anelastic spectra with varying composition, provides evidence against a clear border between rhombohedral and monoclinic phases, and rather confirms the recent structural studies where the two structures are found to coexist over a broad composition range.

Acknowledgments

The authors thank Mr. C. Capianni (ISTEC) for the skillful preparation of the samples, Mr. F. Corvasce (ISC), P.M. Latino (ISC) and A. Morbidini (INAF) for their technical assistance in the anelastic and dielectric experiments.

References

- [1] Jaffe B, Cook W R and Jaffe H 1971 *Piezoelectric Ceramics* (London: Academic Press)
- [2] Damjanovic D 1998 Rep. Prog. Phys. **61** 1267
- [3] Noheda B, Cox D E, Shirane G, Cross L E and Park S -E 1999 Appl. Phys. Lett. **74** 2059
- [4] Frantti J 2008 J. Phys. Chem. B **112** 6521
- [5] Pandey D, Singh A K and Baik S 2008 Acta Cryst. A **64** 192
- [6] Yokota H, Zhang N, Taylor A E, Thomas P A and Glazer A M 2009 Phys. Rev. B **80** 104109
- [7] Viehland D 1995 Phys. Rev. B **52** 778
- [8] Viehland D, Li J -F, Da X and Xu Z 1996 J. Phys. Chem. Sol. **57** 1545
- [9] Ricote J, Corker D L, Whatmore R W, Impey S A, Glazer A M, Dec J and Roleder K 1998 J. Phys.: Condens. Matter **10** 1767
- [10] Woodward D I, Knudsen J and Reaney I M 2005 Phys. Rev. B **72** 104110
- [11] Cordero F, Craciun F and Galassi C 2007 Phys. Rev. Lett. **98** 255701
- [12] Cordero F, Dalla Bella L, Corvasce F, Latino P M and Morbidini A 2009 Meas. Sci. Technol. **20** 015702
- [13] Nowick A S and Berry B S 1972 *Anelastic Relaxation in Crystalline Solids* (New York: Academic Press)
- [14] Franke I, Roleder K, Mitoseriu L, Piticescu R and Ujma Z 2006 Phys. Rev. B **73** 144114
- [15] Amin A, Newnham R E, Cross L E and Cox D E 1981 J. Sol. State Chem. **37** 248
- [16] Fraysse G, Haines J, Bornand V, Rouquette J, Pintard M, Papet P and Hull S 2008 Phys. Rev. B **77** 064109
- [17] Noheda B and Cox D E 2006 Phase Transitions **79** 5
- [18] Noheda B, Cox D E, Shirane G, Guo R, Jones B and Cross L E 2000 Phys. Rev. B **63** 014103

- [19] Glazer A M 1972 Acta Cryst. B **28** 3384
- [20] Corker D L, Glazer A M, Dec J, Roleder K and Whatmore R W 1997 Acta Cryst. B **53** 135
- [21] Kornev I A, Bellaiche L, Janolin P -E, Dkhil B and Suard E 2006 Phys. Rev. Lett. **97** 157601
- [22] Hinterstein M, Schoenau K A, Kling J, Fuess H, Knapp M, Kungl H and Hoffmann M J 2010 J. Appl. Phys. **108** 024110
- [23] Clarke R and Glazer A M 1974 J. Phys. C: Solid State Phys. **7** 2147
- [24] Whatmore R W, Clarke R and Glazer A M 1978 J. Phys. C: Solid State Phys. **11** 3089
- [25] Glazer A M, Thomas P A, Baba-Kishi K Z, Pang G K H and Tai C W 2004 Phys. Rev. B **70** 184123
- [26] Viehland D 2000 J. Appl. Phys. **88** 4794
- [27] Jin Y M, Wang Y U, Khachaturyan A G, Li J F and Viehland D 2003 Phys. Rev. Lett. **91** 197601
- [28] Schönau K A, Schmitt L A, Knapp M, Fuess H, Eichel R -A, Kungl H and Hoffmann M J 2007 Phys. Rev. B **75** 184117
- [29] Rao W -F and Wang Y U 2007 Appl. Phys. Lett. **90** 182906
- [30] Khachaturyan A G 2010 Phil. Mag. **90** 37
- [31] Ahart M, Somayazulu M, Cohen R E, Ganesh P, Dera P, Mao H, Hemley R J, Ren Y, Liermann P and Wu Z 2008 Nature **451** 545
- [32] Frantti J, Fujioka Y and Nieminen R M 2008 J. Phys. Chem. B **111** 4287
- [33] Frantti J, Fujioka Y, Zhang J, Vogel S C, Wang Y, Zhao Y and Nieminen R M 2009 J. Phys. Chem. B **113** 7967
- [34] Vanderbilt D and Cohen M H 2001 Phys. Rev. B **63** 094108
- [35] Fujita K and Ishibashi Y 1997 Jpn. J. Appl. Phys. **36** 254
- [36] Rossetti Jr G A, Khachaturyan A G, Akcay G and Ni Y 2008 J. Appl. Phys. **103** 114113
- [37] Ishibashi Y and Iwata M 1998 Jpn. J. Appl. Phys. **37** L985
- [38] Ishibashi Y and Iwata M 1999 Jpn. J. Appl. Phys. **38** 1454
- [39] Hudak O 2008 Phase Transitions **81** 1073
- [40] Rehwald W 1973 Adv. Phys. **22** 721
- [41] Salje E K H 1990 *Phase transitions in ferroelastic and co-elastic crystals* (Cambridge: Cambridge University Press)
- [42] Rossetti Jr G A, Popov G, Zlotnikov E and Yao N 2006 Mater. Sci. Eng. A **433** 124
- [43] Ragini, Mishra S K, Pandey D, Lemmens H and Van Tendeloo G 2001 Phys. Rev. B **64** 054101
- [44] Atfield J P 2001 Int. J. Inorg. Chem **3** 1147
- [45] Goodenough J B 2004 Rep. Prog. Phys. **67** 1915
- [46] Shannon R D and Prewitt C T 1969 Acta Cryst. B **25** 925
- [47] Lufaso M W, Barnes P W and Woodward P M 2006 Acta Cryst. B **62** 397
- [48] Reaney I M, Colla E L and Setter N 1994 Jpn. J. Appl. Phys. **33** 3984
- [49] Cordero F, Trequattrini F, Deganello F, La Parola V, Roncari E and Sanson A 2010 Phys. Rev. B **82** 104102
- [50] Knudsen J, Woodward D I and Reaney I M 2003 J. Mater. Res. **18** 262
- [51] Glazer A M, Mabud S A and Clarke R 1978 Acta Cryst. B **34** 1060
- [52] Cerereda N, Noheda B, Iglesias T, Fernandez - del Castillo J R, Gonzalo J A, Duan N, Wang Y L, Cox D E and Shirane G 1997 Phys. Rev. B **55** 6174
- [53] Eitel R and Randall C A 2007 Phys. Rev. B **75** 094106
- [54] Leung K, Cockayne E and Wright A F 2002 Phys. Rev. B **65** 214111
- [55] Buixaderas E, Bovtun V, Veljko S, Savinov M, Kuzel P, Gregora I, Kamba S and Reaney I 2010 J. Appl. Phys. **108** 104101
- [56] Tomeno I, Tsunoda Y, Oka K, Matsuura M and Nishi M 2009 Phys. Rev. B **80** 104101
- [57] Ghose Ph, Cockayne E, Waghmare U V and Rabe K M 1999 Phys. Rev. B **60** 836
- [58] Rechav B, Yacoby Y, Stern E A, Rehr J J and Newville M 1994 Phys. Rev. Lett. **72** 1352
- [59] Teslic S, Egami T and Viehland D 1996 J. Phys. Chem. Sol. **57** 1537
- [60] Sicron N, Ravel B, Yacoby Y, Stern E A, Dogan F and Rehr J J 1994 Phys. Rev. B **50** 13168

- [61] Frenkel A I, Frey M H and Payne D A 1999 *J. Synchrotron Rad.* **6** 515
- [62] Moreau J -M, Michel C, Gerson R and James W J 1970 *Acta Cryst. B* **26** 1425